

BIOMATERIALS

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LEUCITE CRYSTALLIZATION FROM $K_2O - Al_2O_3 - SiO_2$ GLASS-FORMING MELTS

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It is shown that the $K_2O - Al_2O_3 - SiO_2$ system is promising for obtaining glass ceramic, containing leucite, for fabricating dental prostheses. Glass formation in this system and the crystallizability of glasses, including glasses modified with Li_2O and Na_2O , is studied. The effect of temperature and the time parameters on liquation and crystallization processes is studied.

Metal ceramic is the most widely used material for dental prostheses because offers better mechanical properties, aesthetics, water resistance, and biocompatibility than other materials.

Metal ceramic dental prostheses consist of a metal cap coated with several layers (at least three) with a special composition. This structural complexity is due to the fact that it is easier to imitate natural teeth, which it is impossible to do with a monolithic material. A multilayer coating also gives good adhesion to a metal substrate.

According to published data (US Patents Nos. 798536, 5944884, 6797048, 5653791, 6761760, 6120591, 4604366; German Patent No. 10310001) the system $K_2O - Al_2O_3 - SiO_2$ is one of the most promising systems for obtaining stomatological glass ceramic facing materials, since it is precisely glass ceramic containing leucite that can serve as a basis for obtaining a material with a CLTE covering a wide range, making it possible to form on metal alloys two- and three-layer coatings with different properties.

Structurally, leucite $K_2O \cdot Al_2O_3 \cdot 4SiO_2$ is a frame silicate with the following computed chemical composition (%²): 21.6 K_2O , 23.3 Al_2O_3 , and 55.1 SiO_2 . Its structural formula is $K[AlSi_2O_6]$, whence it follows that all of the aluminum is built into the silicate structural network as tetrahedra giving a cation : oxygen ratio 0.5 in the aluminum-silicon-oxygen radical. Such frame structures possess high bonding energy, which makes materials based on them mechanically strong and chemically resistant.

But this is not the only advantage of leucite as the main crystalline phase for stomatological facing material in the fabrication of metal ceramic. Since a metal ceramic is deposited on a substrate consisting of metal alloys with high CLTE — $(110 - 150) \times 10^{-7} K^{-1}$, the coating must be matched as closely as possible to it, i.e. its CLTE must be close to that of the alloy. In this respect leucite as a crystalline phase is a quite unique component of glass ceramic. The CLTE of the two polymorphic forms of leucite — cubic high-temperature and tetragonal low-temperature — are $100 \times 10^{-7} K^{-1}$ and $200 \times 10^{-7} K^{-1}$, respectively. This creates real prerequisites for flexible regulation of the CLTE over a wide range, followed by heat treatment of the initial frits by partial conversion of one polymorphic form of leucite into another and by changing the ratio between the residual glassy phase and the crystalline leucite.

In a number of cases, the stomatological porcelain widely used in the production of metal ceramics is synthesized from potassium feldspar, quartz, kaolin, and some additives via a complex physical–chemical interaction of the components of the porcelain paste at high temperature [1, 2]. At 1100–1300°C potassium feldspar transforms into glass, and the remaining components become distributed in the form of a crystalline phase in a high-viscosity melt, as a result of which closed pores appear in the material, lowering the mechanical strength of the coating. Porcelain obtained on the basis of the system $K_2O - Al_2O_3 - SiO_2$ resists acids and alkali and remains biocompatible with tissues in the body for a long period of time (German Patent No. 10310001).

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² Hear and below — the mass content.

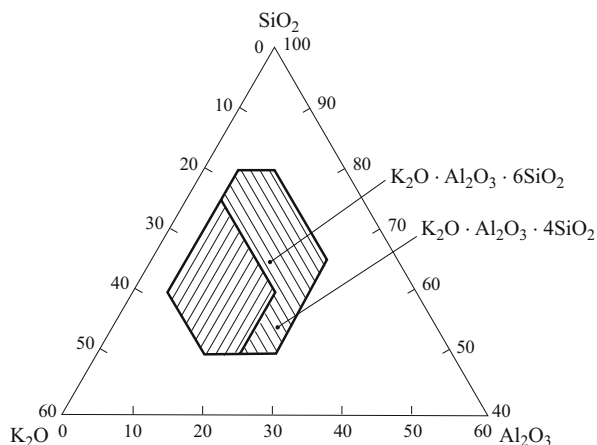


Fig. 1. Region of synthesized compositions in the phase diagram of the system $K_2O - Al_2O_3 - SiO_2$: (hatched) region of vitrified frits; (cross-hatched) region of glasses.

To improve the mechanical properties of leucite-based coatings it is of interest to use glass ceramic technology to obtain glassy crystalline material which enables the formation of a finely dispersed structure with virtually no porosity.

The size of the crystals forming a crystalline phase is very important for obtaining glass crystalline materials with high strength. Preferably, the leucite crystals precipitate in a finely dispersed state with grain size not exceeding $1 - 10 \mu m$, which is the key to obtaining higher strength. Consequently, glass ceramic containing leucite is best obtained not by firing (porcelain technology) but rather by glass ceramic technology based on glassy or vitrified frits.

The existing information on glass formation in the $K_2O - Al_2O_3 - SiO_2$ system and on leucite precipitation from a glassy matrix is fragmentary and unsystematic.

We have studied the glass-forming properties of compositions lying in the leucite crystallization field in the $K_2O - Al_2O_3 - SiO_2$ system. The glass compositions were projected onto the field of crystallization of leucite and, partially, potassium feldspar (Fig. 1).

The experimental glasses were made using two regimes:

in a gas furnace at temperature $1450 \pm 10^\circ C$ with holding time 2 h at maximum temperature; the total glassmaking time was about 6 h;

in an electric furnace at temperature $1340 \pm 10^\circ C$ with holding time 3 h.

The glass quality was evaluated according to the degree of founding and fining.

Glasses with 20% and more K_2O , even approaching the stoichiometric point of leucite, where the liquidus temperatures are quite high, were completely found and fined. Compositions containing 10–20% K_2O are well-vitrified but opaque frits, which is evidenced by the incompletely reacted silica and inadequate fining. The melts obtained were all distinguished by very high viscosity during production.

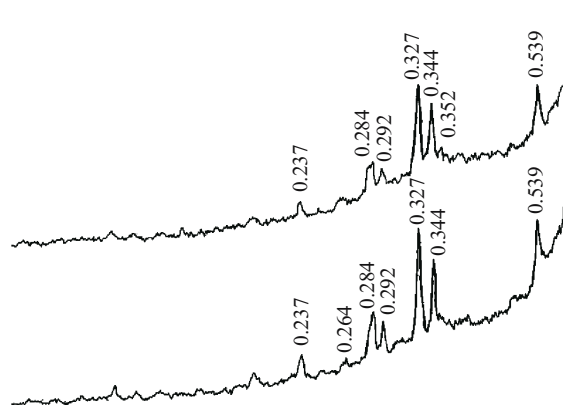


Fig. 2. X-ray diffraction patterns of crystallized samples with addition of 5% (a) and 10% (b) Li_2O (leucite peaks).

It is interesting that transparent glass actively forms on the basis of compositions in the crystallization field of leucite with liquidus temperatures $1100 - 1500^\circ C$ while compositions in the crystallization field of potassium feldspar with liquidus temperatures $800 - 1000^\circ C$ do not give transparent glasses but only vitrified frits. This is probably due to the kinetic conditions of glass formation and the elevated content of SiO_2 in the glass.

A study of the crystallizability of the obtained glasses and frits in 1 h at temperatures $600 - 1100^\circ C$ shows that the glassy state of the synthesized compositions is highly stable, which is evidenced by the complete absence, because of the very high viscosity of the glasses, of any indications of their crystallization.

Consequently, to decrease the viscosity, glasses to which lithium and sodium oxides were added in amounts of 5 and 10% instead of SiO_2 were synthesized. Under the same conditions of synthesis such compositions were well-founded and fined. The facts that Na_2O can become partially embedded in the crystal lattice of leucite, forming solid solutions in the pseudobinary system $K_2O \cdot Al_2O_3 \cdot 4SiO_2 - Na_2O \cdot Al_2O_3 \cdot 4SiO_2$, while a substantial region of metastable liquation is present in the lithium–aluminum–silicate system, which promotes devitrification, were taken into account.

The glasses obtained were subjected to two-step heat treatment in accordance with the technology of glass ceramics, i.e., the first step is high-temperature treatment to form the centers of crystallization and the second step (conducted at a lower temperature) promotes crystal growth on the centers which have appeared. Such a scheme also presupposed that metastable liquation phenomenon occur, especially in the presence of Li_2O , at the first heat-treatment step.

Heat treatment of glasses with Li_2O added according to the scheme indicated above yields a crystalline phase — high-temperature cubic leucite, which was detected by x-ray diffraction measurements performed with a DRON-3 diffractometer (Fig. 2).

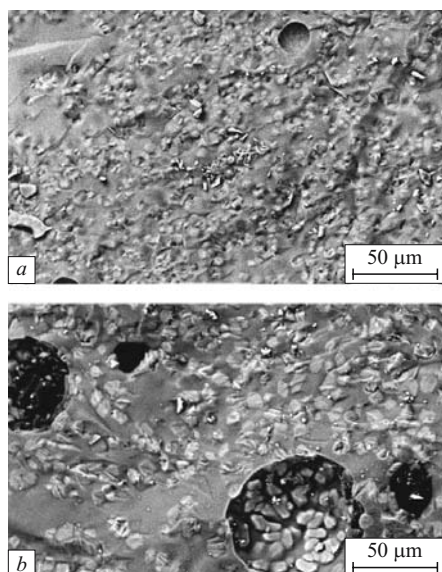


Fig. 3. Electron-microscope photographs of crystallized leucite-containing glasses with 5% (a) and 10 % (b) Li_2O .

The diffraction peaks in the x-ray patterns obtained completely correspond to the tabulated values for leucite. The number of leucite crystals increases with increasing Li_2O content, as is evidenced by the increase in the intensity of the reflections.

Characteristically, in the presence of Li_2O leucite precipitates from compositions which initially lie in the crystallization field of potassium feldspar (70 – 80% SiO_2). Replacing Si_2O with Li_2O shifts the position of the initial compositions into a region with less high-silica (65 – 70% SiO_2), corresponding to the primary crystallization of leucite. Potassium feldspar could have appeared only as a secondary crystalline phase (in accordance with the crystallization paths for melts), but the precipitation of this phase was not determined.

A crystalline phase does not form at all when SiO_2 is replaced with Na_2O during heat treatment of glasses. It is entirely likely that active precipitation of leucite in the presence of Li_2O is due not only to the larger decrease of the viscosity of glasses but also a higher probability for the development of metastable liquation phenomena.

Figure 3 displays electron-microscope photographs of the structure of crystallized lithium-containing glasses. These photographs were obtained with a JEOL JSM-5610 LV scanning electron microscope. It was determined that a fine crystalline structure forms with the addition of 5% and 10% Li_2O . In addition, the sizes of the crystals increase with increasing Li_2O content from 1 – 2 μm (5% Li_2O) to 10 μm (10% Li_2O). For 10% Li_2O distinct liquation drops are observed in the samples, as compared with glasses containing 5% Li_2O .

TABLE 1.

Elemental and oxide compositions of crystals				Theoretical leucite composition, %
element	mass content, %	oxide	mass content, %	
<i>Glasses containing 5% Li₂O</i>				
O	46.77	—	—	—
Al	10.78	Al ₂ O ₃	20.36	23.3
Si	30.49	SiO ₂	65.23	55.1
K	11.96	K ₂ O	14.41	21.6
<i>Glasses containing 10% Li₂O</i>				
O	43.23	—	—	—
Al	10.96	Al ₂ O ₃	20.72	23.3
Si	25.79	SiO ₂	55.16	55.1
K	20.02	K ₂ O	24.12	21.6

Data from elemental x-ray microanalysis of the crystals obtained are displayed in Table 1 (neglecting the lithium content, which being a light element is not determined by x-ray microanalysis). The theoretical composition of leucite is also presented for comparison.

Even though x-ray phase analysis in both cases shows precipitation of leucite on crystallization, microanalysis of the composition of the crystals shows differences. For 10% Li_2O the composition of the crystals precipitated in the glass is close to the theoretical composition for leucite. An elevated content of SiO_2 is observed in glasses with 5% Li_2O but probably because of distortions from the residual glass phase which surrounds them. The results of the microanalysis of the composition of the crystals suggest that Li_2O remains completely in the residual glassy phase.

In summary, as a result of the high stability of the glassy state of compositions lying in the crystallization field of leucite, precipitation of leucite crystals during heat treatment from glass-forming compositions in the $\text{K}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ system occurs only with additional introduction of oxides which not only lower the viscosity of melts (for example, Li_2O and Na_2O) but also promote the development of metastable liquation phenomena (Li_2O), owing to the fact that a volume-crystallized fine crystalline structure forms on crystallization.

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